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ONLINE: WPI AND CLAIMS

(54) Catalytic system and process for producing synthesis gas by reforming light hydrocarbons with CO$_2$

(57) A catalytic system for the production of synthesis gas by reacting light hydrocarbons, preferably methane, with CO$_2$ is described formed from:

- one or more compounds of metals of the platinum group, preferably chosen from rhodium, ruthenium and iridium;
- a support consisting of inorganic compounds chosen from oxides and/or spinels of aluminium, magnesium, zirconium, silicon, cerium and/or lanthanum, possibly in the presence of alkaline metals,

in which the weight percentage of the metal or metals of the platinum group in the catalytic system is between 0.01 and 20%, and preferably between 0.1 and 5%.
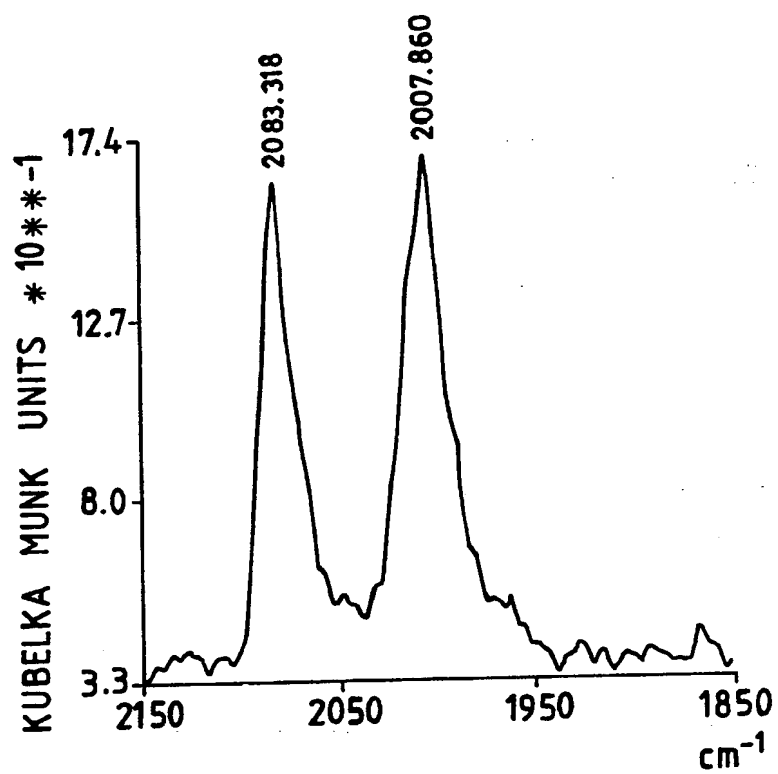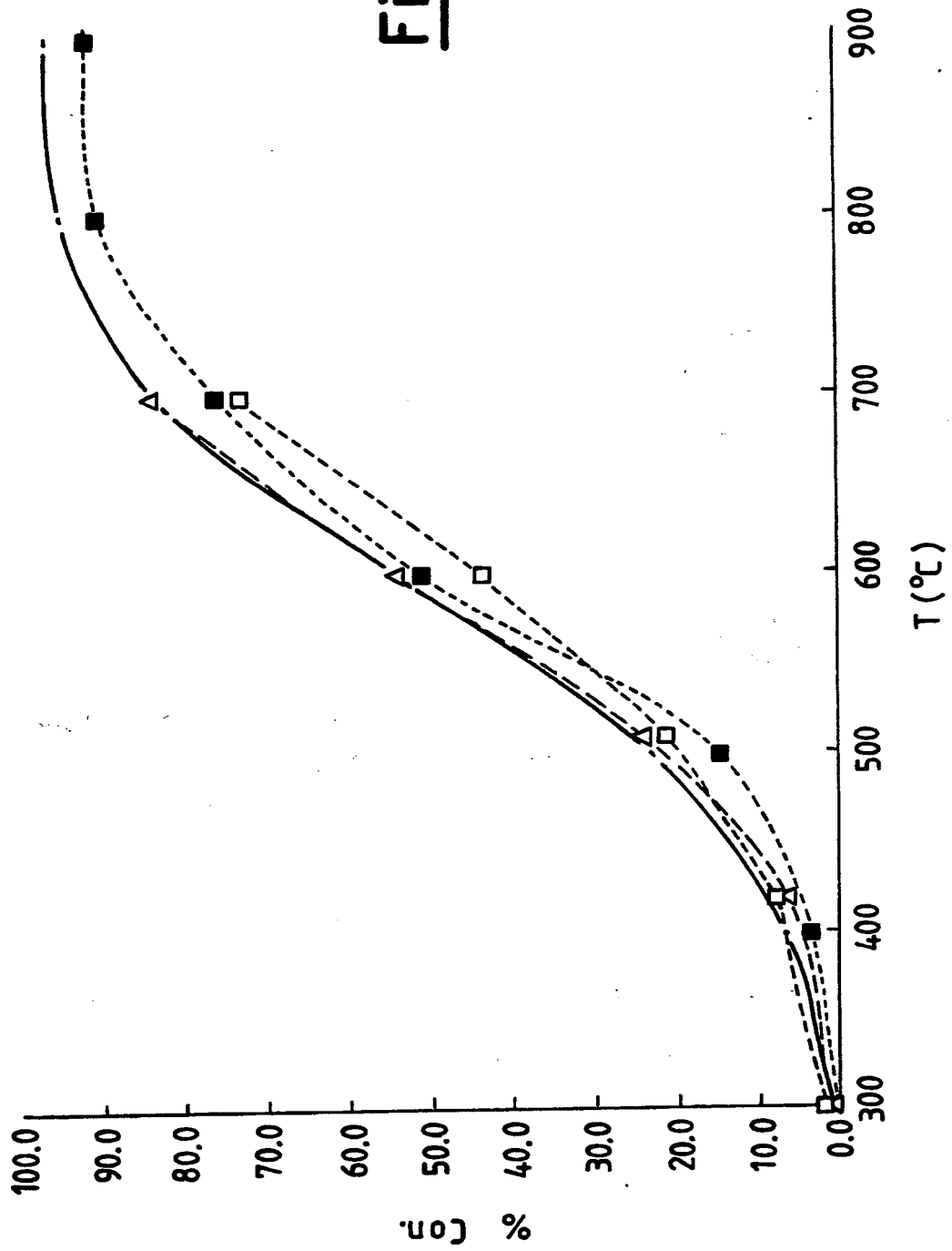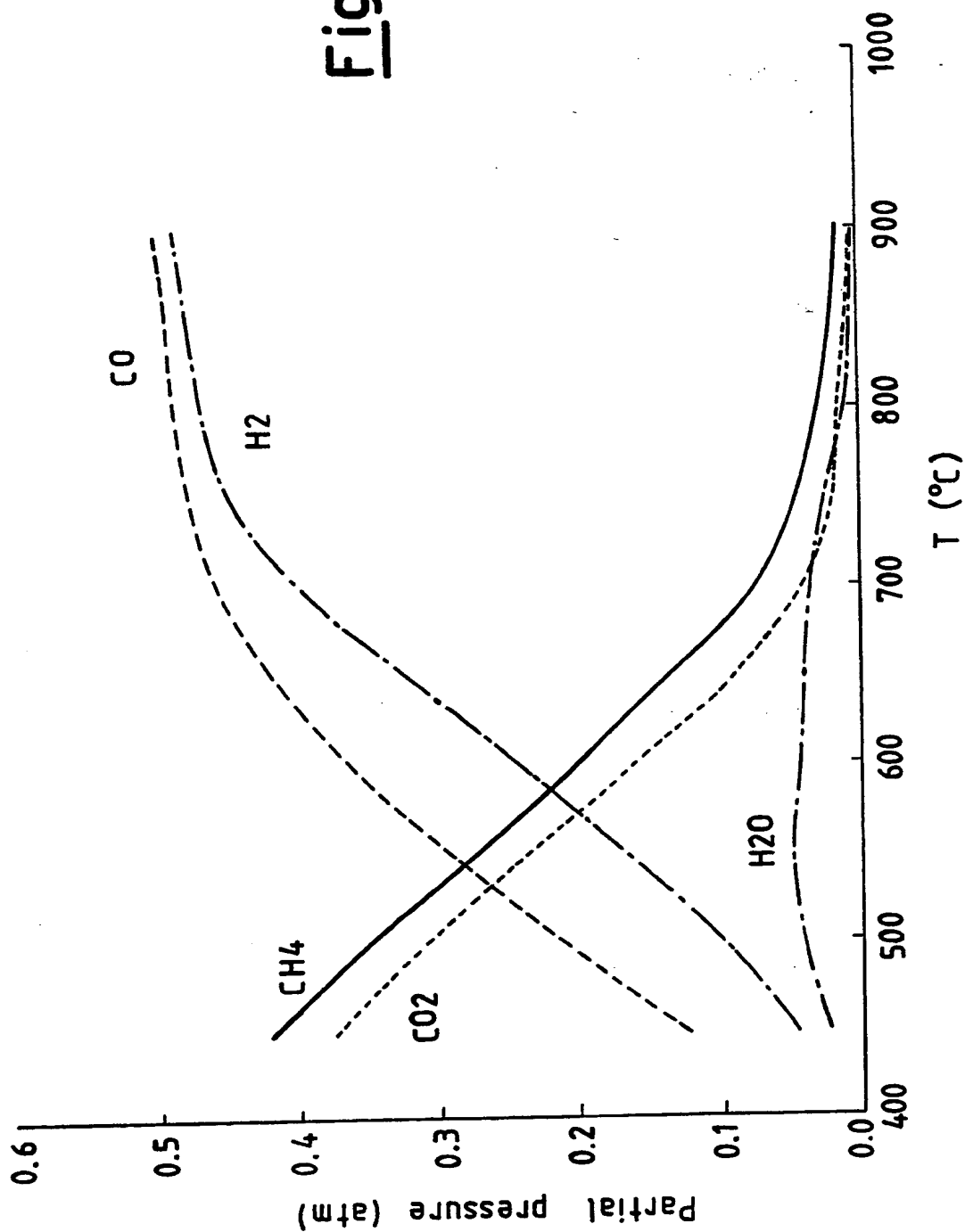
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Fig.1

Fig.2

Fig.3

CATALYTIC SYSTEM AND PROCESS FOR PRODUCING SYNTHESIS GAS BY
REFORMING LIGHT HYDROCARBONS WITH CO2

This invention relates to a catalytic system and its use in a

5 reforming process for the single-stage production of a gaseous

mixture of H2 and CO.

The main reactants used are CO2 and light hydrocarbons, preferably

methane. The chemical equation describing the process of the

present invention is:

10 $$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2 \qquad (1)$$
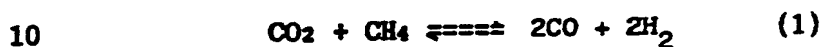
Hydrocarbon reforming reactions using CO2 have certain

considerable advantages compared with the widespread steam

reforming processes described by the chemical equation:

$$H_2O + CH_4 \rightleftharpoons CO + 3H_2 \qquad (2)$$

15 Processes mainly using reaction (1) represent the best method for

producing mixtures of H2 and CO if the natural gas used as the

feedstock contains large CO2 quantities.

In addition an H2/CO mixture in a ratio close to 1, as can be

easily obtained by this invention, can be used advantageously in

20 alcohol synthesis and in oxosynthesis. Currently, using syngas

produced by the steam reforming reaction (2), the obtained H2/CO

mixture has a ratio ≥ 3. To obtain smaller ratios a second stage

has to be used employing the reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (3)$$
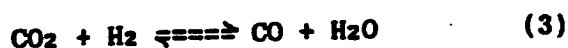
Adjusting the CO/H_2 ratio by this chemical reaction negatively affects the overall economy of the process.

5   A potential use of a reforming process using CO_2 as the main reactant instead of steam is in Fischer-Tropsch synthesis plants in which the CO_2 and methane produced could be again recycled to syngas of low H_2/CO ratio.

The reforming process described by reaction (1), which produces

10   H_2/CO mixtures in an approximately equimolecolar ratio in a single stage, can also be advantageously used in highly integrated plants for ferrous mineral reduction.

Finally, methane reforming processes employing CO_2 can be advantageously used, compared with steam reforming reactions, in

15   thermal cycles for energy storage and transport by thermochemical pipe (TCP) [see T.A. Chubb, Solar Energy, 24, (1980) 341].

However, in contrast to steam reforming, systems involving H_2 and CO synthesis from CO_2 and from light hydrocarbons do not have a well defined technology behind them. The Ni-based catalysts usually used in

20   steam reforming processes are not sufficiently selective, and deactivate rapidly when the H_2O/C ratio is less than 2 [see R.E. Reitmeier, K. Atwood, H.A. Bennet Jr. and H.M. Baugh, Ind. Eng. Chem. 40 (4), 620 (1948)].

This deactivation is due to the formation of carbon, which covers

25   the active metal centres during catalysis and accumulates in the catalyst pores, possibly causing fragmentation.

A catalytic system has now been found which produces synthesis gas

(H₂ and CO) by a light hydrocarbon reforming reaction without undergoing any discernible deactivation due to coke formation by the reactions:

$$2CO \longrightarrow CO_2 + C$$

5 $$CH_4 \longrightarrow 2H_2 + C$$
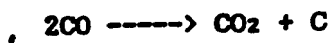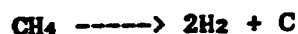
even if the H₂O/C ratio is distinctly favourable to such formation.

The catalytic system according to the present invention is characterised by being formed from:

10 - one or more compounds of metals of the platinum group, preferably chosen from rhodium, ruthenium and iridium;

- a support consisting of inorganic compounds chosen from oxides and/or spinels of aluminium, magnesium, zirconium, silicon, cerium and/or lanthanum, either alone or in mutual combination

15 and possibly in the presence of alkaline metals,

in which the weight percentage of the metal or metals of the platinum group in the catalytic system is between 0.01 and 20%, and preferably between 0.1 and 5%.

The supports used can also consist of silicified aluminium,

20 magnesium, cerium or lanthanum oxides.

The surface area of the catalysts used preferably varies between 1 and 400 m²/g and more preferably between 10 and 200 m²/g, while the pore volume preferably varies between 0.1 and 3 cc/g and more preferably between 0.5 and 2 cc/g.

25 The catalytic system can be obtained either by impregnating the inorganic compounds with a solution of a salt of the metals of the platinum group followed by thermal drying and calcining, or by

dispersing the inorganic compounds in an organic solvent, then reacting this in a carbon monoxide or inert atmosphere with solutions of compounds of the metals of the platinum group. In this second case, the generally exothermic reaction, which

5 results in coloured reaction products, is followed by filtration, drying and calcining.

More particularly, the catalytic system in question can be. prepared by heterogeneous solid-liquid reaction at a temperature of between 0°C and 150°C, and preferably between 20°C and 50°C,

10 between compounds of the metals of the platinum group dissolved in an organic solvent and the stated inorganic compounds dispersed in the same solvent.

Following this procedure, the metal quantity which fixes to the substrate is determined mainly by the chemical properties of the

15 inorganic oxide rather than by its porosity and surface area. These latter are however important with respect to the integrity and stability of the catalyst during the reforming reaction. In this respect, the accumulation of carbon in too small pores leads to material fragmentation. A reduced support surface area also

20 results in a lesser dispersion of metal and favours sinter phenomena with consequent catalyst deactivation.

The method for preparing supports consisting of silicified aluminium, magnesium, cerium or lanthanum oxides consists essentially of a condensation reaction between the inorganic oxide

25 (of aluminium, magnesium, cerium or lanthanum) and a silicon compound containing hydrolyzable organic groups, followed by removal of the unhydrolyzed organic residues by combustion or

reaction in the presence of steam.

Using such silicification methods, materials can be obtained
containing percentages of silicon varying between 0.5 and 15% and
preferably between 1 and 5% by weight.

5   The present invention also provides a catalytic reforming process
for light hydrocarbons, preferably methane, which enables mixtures
of H_2 and CO to be obtained in / molecular ratios varying between 0.6 and
6, and preferably between 0.8 and 3.

This catalytic process is characterised by conducting the

10   reforming preferably in a single stage using the aforedescribed
catalytic system and operating at a temperature of between 350°C
and 850°C, and preferably between 550°C and 750°C, at a pressure
of between 0.5 and 50 atm, and preferably between 1 and 40 atm.

If methane is used, the required volumetric CO_2/CH_4 reactant ratio

15   is between 0.5 and 15, and preferably between 0.8 and 10.

Under all these thermodynamic conditions the process can also be
conducted in the presence of steam, if the particular application
of the product synthesis gas requires it.

In this respect, it is necessary only to adjust the relative CO_2

20   and H_2O feed quantities to obtain a synthesis gas with any desired
H_2/CO ratio from 1 to 6.

Although the process is particularly suitable for methane
reforming reactions, any other light hydrocarbon or mixture can be
used in the process.

25   For example C_1-C_4 paraffins and olefins can be used by suitably
choosing optimum temperature and pressure conditions and CO_2
ratios.

Any natural gas containing hydrocarbon mixtures in which the methane content preferably exceeds 80% by volume can be used. Some examples are given below to better illustrate the invention, which however is not to be considered limited by them or to them.

5 EXAMPLE 1

Catalyst preparation

The inorganic oxide used as the support was prepared by the following procedure.

A commercial magnesium oxide (supplied by Carlo Erba) with a

10 surface area of 210 m²/g was suspended under stirring in a tetraethylsilicate (TES) solution. The temperature was maintained between 80°C and 90°C to favour evaporation of the ethanol formed by the condensation reactions. A dry gaseous nitrogen stream was fed into the reaction environment. Gas chromatograph analysis of

15 the exit gas showed the formation of ethanol.

The condensation reaction was considered at an end when ethanol was no longer detected in the exit gas stream. At this point the temperature was raised to 180°C to distil off the unreacted TES. The unreacted ethoxy groups bonded to silicon atoms anchored to

20 the solid inorganic support were then hydrolyzed by feeding a stream of nitrogen and steam at 200°C. Ethanol was also detected in the gas stream during this step. Infrared spectrum analysis on the material obtained up to this point shows the presence of numerous hydroxyl bands which were not present in the starting

25 material. The solid was then heated to 850°C (5°C/min) and maintained at this temperature for 10 hours. After this treatment the surface area had reduced to 32m²/g, the silicon content being

1.5% by weight. Differential thermal, thermogravimetric and
infrared spectroscopic analysis conducted during three cycles at
temperatures between 25°C and 750°C showed no significant
alteration in the physico-chemical properties of the silicified

5 materials obtained. 50 g of silicified magnesium oxide were then
suspended in 100 ml of 2-methylpentane in a nitrogen atmosphere.
A second solution of 50 ml of the same solvent containing 0.91 g
of $Rh_4(CO)_{12}$ in a CO atmosphere was dripped rapidly into the
silicified oxide suspension under stirring. The organic solution

10 decolours rapidly passing from intense red to colourless, with the
white solid simultaneously colouring. It is filtered in an inert
atmosphere to obtain a material containing 1% by weight of Rh in r
highly dispersed condition, as could be deduced from an analysis
of the vibrational carbonyl bands of the surface complexes (see

15 Figure 1 showing the diffused reflectance spectrum obtained on the
pulverulent solid, in which the horizontal axis represents the
wave number in cm^{-1} and the vertical axis represents Kubelka Munk
intensity units). The transformations of the surface complexes
during thermal reduction with hydrogen in gaseous CH_4 and CO_2

20 atmospheres were also studied by infrared spectroscopy. This
resulted in a satisfactory understanding of surface nucleation
phenomena, ensuring high reproducibility in material preparation.

Reforming reaction

The reforming reaction was conducted in a fixed bed quartz reactor

25 containing 3 cc of catalyst by feeding a gaseous equimolecular stream
of CH_4 and CO_2 at a pressure of one atmosphere. In-line gas
chromatograph analysis was carried out on the exit gas stream

starting from 300°C and continuing until 750°C. The gas hourly

space velocity was maintained at 1000 (1/kg·h).

Figure 2 shows the various experimental CH_4 and CO_2 conversion

values at the various temperatures investigated (shown by black

5   squares and dots respectively). The same figure also shows the

theoretically calculated conversion values for the equilibrium

system for the reactions:

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2$$

(A)

10    $$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

The theoretical conversion of CO_2 at equilibrium is shown by

triangles, and that of CH_4 by white squares.

From the results obtained it can be deduced that the catalyst is

extremely active and enables conversions close to the

15   thermodynamic equilibrium conversions to be obtained within the

temperature range studied. The H_2O percentage in the reaction

product mixture is also close to the values calculated for the

system (A) at equilibrium. Figure 3 shows the theoretically

calculated variations in the concentrations of the gaseous species

20   with temperature for the system under examination at a total

pressure of 1 atm. The experimentally obtained gaseous species

concentrations faithfully reproduce this pattern.

The H_2/CO ratio within the range of 650-750°C was slightly less

than 1.

25   Table 1 shows the results obtained for catalytic tests lasting 100

hours at 700°C conducted with the catalysts described in Examples

1-4 and 6, compared with the results obtained using a commercial

steam reforming catalyst (Example 7) containing approximately 15.5% of Ni supported on α-alumina.

During the tests, catalysts comprising Rh deposited on silicified magnesium oxide proved to be extremely active in catalyzing the

5 reactions of the system (A) but, surprisingly, not in catalyzing the carbon formation reactions even where these are favoured under these conditions.

The results of quantitative carbon analysis on the discharged catalysts are shown in Table 1. During the 100 hours the activity

10 and selectivity of the catalytic system remained constant.

EXAMPLE 2

The catalyst synthesis procedure described in Example 1 was repeated but using a solution containing 1.05 g of $Ru_3(CO)_{12}$ to obtain a solid containing 1% of Ru by weight.

15 The reforming reaction was conducted as in Example 1 feeding the same reactant mixture under the same pressure and spatial velocity conditions at temperatures of between 300°C and 750°C. Again in this case the CH_4 and CO_2 conversions are close to equilibrium values even if slightly less than those obtained in Example 1 (see

20 Table 1).

EXAMPLES 3-4

In these cases the catalysts used contained the noble metals Rh (Example 3) or Ru (Example 4) and silicified alumina. This latter was prepared by condensing tetraethylsilicate with a gamma alumina

25 supplied by AKZO in accordance with the procedure described in Example 1. The catalytic systems thus obtained proved to possess the same characteristics as those described in Examples 1 and 2,

ie active in catalyzing the reactions of the system (A) within the
entire temperature range investigated but inactive in catalyzing
the reactions involved in the formation of carbon on the catalyst.
Table 1 also shows the results obtained during 100 hour catalytic

5 tests in these two cases.

EXAMPLE 5

In this case the reactants were a gaseous stream of C_2H_6 and CO_2
in a 1/2 ratio. The catalytic tests were conducted at
temperatures between 400°C and 700°C using the catalyst of Example

10 2. The ethane conversion/during a catalytic test lasting 100
at 700°C
hours was found to be 100% and the CO_2 conversion 98%. The H_2/CO
ratio was 0.7. The methane in the exit gas was less than 3%.

EXAMPLE 6

In this example the catalyst synthesis procedure described in

15 Example 1 was modified in that the noble metal was deposited on
the silicified oxide by an impregnation reaction conducted by
dripping an aqueous solution of Rh nitrate onto the silicified
oxide until it was just soaked. The catalyst obtained in this
manner contained 1% (wt/wt) of Rh. In this case the catalytic

20 tests conducted as in Examples 1-5 showed that the material
modifies its characteristics during the first 10 hours of reaction
at 700°C. During this period the conversion values increase until
they settle down at the values shown in Table 1.
However after the induction period the characteristics of the

25 catalytic systems described in Examples 1-4 are again obtained in
this case.

EXAMPLE 7 - Comparative

Compared with Example 1 a commercial steam reforming catalyst consisting of about 15.5% by weight of Ni supported on alumina was used.

The results obtained are shown in Table 1.

TABLE 1

	%conv CO_2	% conv CH_4	sel. *	H_2/CO (mol/mol)	mg C/g cat (100 h)
Ex.1	84.1	73.4	96.2	0.87	< 0.5
Ex.2	75.6	68.3	97.1	0.90	0.5
Ex.3	81.4	70.1	96.0	0.85	< 0.5
Ex.4	71.5	63.7	96.7	0.88	0.8
Ex.6	81.2	70.8	96.0	0.85	0.7
Ex.7	68.5	64.3	85.2	0.92	65.2

* (moles CO + H_2)/(moles CO + H_2 + H_2O + C).100

CLAIMS

1. A catalytic system for the production of synthesis gas by reforming hydrocarbon with CO_2, comprising:

one or more compounds of a platinum group metal; and

a support comprising an inorganic compound chosen from oxides and/or spinels of aluminium, magnesium, zirconium, silicon, cerium and/or lanthanum, either alone or in combination;

in which the weight of the platinum group metal or metals in the catalytic system is from 0.01 to 20%.

2. A catalytic system as claimed in claim 1, wherein the weight percentage of the platinum group metal or metals is from 0.1 to 5%.

3. A catalytic system as claimed in claim 1 or 2, wherein the platinum group metal is rhodium, ruthenium or iridium.

4. A catalytic system as claimed in any of claims 1 to 3, having a surface area of from 1 to 400 m^2/g and a pore volume of from 0.1 to 3 cc/g.

5. A catalytic system as claimed in claim 4, having a surface area of from 10 to 200 m^2/g and a pore volume from 0.5 to 2 cc/g.

6. A catalytic system as claimed in any of claims 1 to 5, wherein the support comprises silicified aluminium, magnesium, cerium or lanthanum oxide.

7. A catalytic system as claimed in any of claims 1 to 6, further comprising one or more alkali metals or alkaline earth metals on the support.

8. A catalytic system as claimed in claim 12, substantially as hereinbefore described.

9. A process for producing synthesis gas by reforming hydrocarbon with CO_2, wherein the reforming is carried out in the presence of a catalytic system as claimed in any of claims 1 to 8, at a temperature of

from 350°C to 850°C and at a pressure of from 0.5 to 50 atm.

10. A process as claimed in claim 9, wherein the temperature is from 550 to 750°C and the pressure is

5 from 1 to 40 atm.

11. A process as claimed in claim 9 or 10, wherein the reforming is conducted in a single stage.

12. A process as claimed in any of claims 9 to 11, wherein the volumetric CO_2/hydrocarbon ratio is from

10 0.5 to 15.

13. A process as claimed in claim 12, wherein the volumetric CO_2/hydrocarbon ratio is from 0.8 to 10.

14. A process as claimed in any of claims 9 to 12, wherein steam is present to such an extent that the

15 H_2/CO ratio is from 1 to 6.

15. A process as claimed in claim 9, wherein the hydrocarbon is methane.

16. A process as claimed in claim 9, substantially as hereinbefore described.

20 17. Synthesis gas produced by a process as claimed in any of claims 9 to 16.